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US]; 2301 Brazosport Blvd., Patent Department, B-1211,
Freeport, TX 77541 (US).(72) Inventors: PARIKH, Deepak, R. ; 59 North Trillium
Court, Lake Jackson, TX 77566 (US). CARDWELL, Ro-
bert, S. ; 106 Any Way, Lake Jackson, TX 77566 (US).
KOLTHAMMER, Brian, W., S. ; 54 Royal Oak Circle,
Lake Jackson, TX 77566 (US).(74) Agent: WHITE, L., Wayne; The Dow Chemical Company,
Patent Dept., B-1211, Freeport, TX 77541 (US).(81) Designated States: CA, FI, JP, KR, European patent (AT,
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(54) Title: ETHYLENE INTERPOLYMER POLYMERIZATIONS

(57) Abstract

A new process of interpolymers ethylene interpolymers products having improved properties, such as increased onset of crystallization temperature, is disclosed. Preferably, the process comprises interpolymers a first homogeneous ethylene/alpha-olephin interpolymers and at least one second homogeneous ethylene/alpha-olephin interpolymers using at least two constrained geometry catalysts having different reactivities such that the first ethylene/alpha-olephin interpolymers has a narrow molecular weight distribution (NMWD) with a very high comonomer content and relatively high molecular weight and the second ethylene/alpha-olephin interpolymers has a NMWD with a low comonomer content and a molecular weight lower than that of the first interpolymers. The resultant first homogeneous interpolymers is combined with the resultant second homogeneous interpolymers in appropriate weight ratios resulting in the desired finished polymer structure. The first interpolymers and the second interpolymers can be polymerized in a single reactor or they can be polymerized in separate reactors operated in parallel or series.

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ETHYLENE INTERPOLYMER POLYMERIZATIONS

This invention relates to processes of manufacturing ethylene interpolymer products which have improved properties, especially increased onset of crystallization temperature. The ethylene interpolymer products are made by a polymerization with two or more constrained geometry catalysts having varying reactivities. The interpolymer products can also be made by polymerization reactions in two or more separate, parallel reactors, with the resultant interpolymers intimately combined.

Thermoplastic polymers can be classified as semi-crystalline (at least partly crystalline), highly crystalline, or wholly or mainly amorphous. Crystalline or semi-crystalline polymers typically have a distinct melting point, as measured by differential scanning calorimetry (DSC). Crystalline and semi-crystalline polymers are typically melt-processed into fibers, films or molded articles.

Controlling the nucleation and crystallization rates of the polymers during melt processing is important in determining the physical properties of the finished article. Various methods of controlling nucleation and crystallization have been attempted, usually incorporating nucleating agents (for example, inactive (physical) or active (chemical)) or completely changing polymers. Physical nucleating agents are typically finely divided particles and have a melting and freezing temperature greater than that of the polymer in which the particles are utilized while the chemical nucleating agents are primarily combinations of acidic and basic compounds such as organic or inorganic compounds. Unfortunately, the particulate nucleating agents can also detrimentally affect the physical properties of the final product, for example by lowering the tensile strength of film made from the polymers.

Copending Application Serial Number 07/609,286, filed November 5, 1990, has solved this particulate nucleation problem by blending linear polyethylene with other polyethylenes to cause the blend to have an increased onset of crystallization. While this process is effective, economic considerations can also affect the ability of polymers to be melt blended cost effectively.

Many methods of polymerizing polymers and forming polymer blends to do specific jobs are disclosed in the literature. For example, U.S. Patent 4,937,299 (Ewen et al.) teaches the use of a homogeneous catalyst system comprising at least two different mono-, di- or tricyclopentadienyls and their derivatives of a Group 4b, 5b and 6b transition metal each having different reactivity ratios and aluminoxane. The catalyst system is described as being homogeneous in a solution polymerization system and that the soluble (i.e., homogeneous) catalyst can be converted to a heterogeneous catalyst system by depositing it on a catalyst support. Thus, U.S. Patent 4,937,299 describes their homogeneous catalyst system as a soluble catalyst system.

International Patent Application Number PCT/US89/04259 (Stehling et al.) discloses linear ethylene interpolymer blends of interpolymers having narrow molecular weight distributions and narrow composition distributions. The components of the blends are said to have narrow molecular weight distributions (i.e., the ratio of the weight average molecular weight to the number average molecular weight is less than or equal to 3.0). The components are said to be prepared by using metallocene catalyst systems known to provide narrow composition distributions and narrow molecular weight distributions. The desirable molecular weight and composition distributions are said to be obtained by blending different components or by polymerization of the blend components in the same or multiple reactors.

A new ethylene polymerization process has now been discovered to produce ethylene polymer products having many improved properties, including increased onset of crystallization temperature.

The ethylene polymerization process comprises the steps of:

(a) polymerizing a first homogeneous ethylene polymer using a first activated constrained geometry catalyst composition having a first reactivity such that the first polymer has a melt index of from 0.05 to 50 grams/10 minutes,

(b) polymerizing at least one second homogeneous ethylene polymer using a second activated constrained geometry catalyst composition having a second reactivity such that the second ethylene polymer has a melt index of from 0.05 to 50 grams/10 minutes, and

(c) combining from 50 to 95 weight percent of the first ethylene polymer with from 5 to 50 weight percent of the second ethylene polymer to form an ethylene polymer product.

Preferably, the homogeneous ethylene polymers are ethylene/alpha-olefin interpolymers.

The polymerized ethylene and interpolymerized ethylene/alpha-olefin products have increased onset of crystallization temperature as well as improved cling and low hexane extractables when converted to film form.

The activated constrained geometry catalyst compositions used in the interpolymerization process of the present invention can be made and injected separately into

separate polymerization reactors, or, preferably, injected separately into the same polymerization reactor, or, especially, they can be injected together into the same polymerization reactor.

Figure 1 shows a differential scanning calorimetry melting curve for a homogeneous interpolymer of the present invention.

Figure 2 shows a differential scanning calorimetry melting curve for a comparative heterogeneous polymer.

The homogeneous polymers and interpolymers of the present invention are herein defined as defined in USP 3,645,992, the disclosure of which is incorporated herein by reference. Accordingly, homogeneous interpolymers are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer, whereas heterogeneous interpolymers are those in which the interpolymer molecules do not have the same ethylene/comonomer ratio.

In addition, the homogeneous interpolymers of the present invention have a melting curve which resembles that depicted in Figure 2 (i.e., a single melting peak), as opposed to the multiple melting peak demonstrated by a comparative heterogeneous polymer shown in Figure 3.

The homogeneous polymers used to make the novel polymer products of the present invention can be ethylene homopolymers or, preferably, interpolymers of ethylene with at least one C_3 - C_{20} α -olefin and/or C_4 - C_{18} diolefins. The homogeneous interpolymers of the present invention can also be interpolymers of ethylene with at least one of the above C_3 - C_{20} α -olefins and/or diolefins. The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like. That is, at least one other comonomer is polymerized with ethylene to make the interpolymer. Therefore, in another aspect, the invention is a process for preparing an ethylene/ α -olefin terpolymer product, comprising the steps of:

(a) interpolymerizing ethylene, a first comonomer and a second comonomer to form a homogeneous terpolymer using a first activated constrained geometry catalyst composition having a first reactivity and a second activated constrained geometry catalyst composition having a second reactivity to form an ethylene/ α -olefin terpolymer product, and

(b) recovering the ethylene/ α -olefin terpolymer product.

Other unsaturated monomers usefully polymerized according to the present invention include, for example, ethylenically unsaturated monomers, conjugated or nonconjugated dienes, polyenes, etc. Preferred monomers include the C_2 - C_{10} α -olefins especially ethylene, 1-propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes,

tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, and naphthenics (for example, cyclopentene, cyclohexene and cyclooctene).

The density of the homogeneous polymers used to make the novel interpolymer products of the present invention can be any density appropriate to the selected end use application, for example higher density products for higher modulus applications. Preferably the density is from 0.88 grams/cubic centimeter (g/cm^3) to 0.965 g/cm^3 . Density measurements are determined herein according to ASTM D-792.

The molecular weight of the homogeneous polymers used to make the novel polymer products of the present invention is usually indicated and measured by melt index. The melt index is according to ASTM D-1238, Condition (E) (i.e., 190°C/2.16 kilograms) and is also known as I_2 . The I_2 of the homogeneous polymers used to make the novel interpolymer products of the present invention can also be convenient to the chosen end use application, but preferably is from 0.01 grams/10 minutes to 1000 g/10 minutes.

The melt flow ratio is indicated and measured by I_{10}/I_2 according to ASTM D-1238, Conditions (N) (190°C/10 kilograms) and (E), respectively. The I_{10}/I_2 of the novel polymer products of the present invention can also be conveniently chosen specific to the desired end use application, but preferably is from 6 to 16. Accordingly, the I_{10}/I_2 ratios of the specific homogeneous polymers used to make up the novel interpolymer products can be appropriately selected.

The first process disclosed herein for producing the novel interpolymer products is also effective when using at least two reactors, especially when a first reactor and a second reactor are operated in series, i.e., one after the other. The first process is also particularly effective when both the ethylene copolymers of (a) and (b) are ethylene/alpha-olefin interpolymers.

A preferred interpolymerization process of the present invention comprises the steps of:

(a) polymerizing a first homogeneous ethylene/alpha-olefin interpolymer using a first constrained geometry catalyst having a first reactivity such that the first interpolymer has from 5 to 30 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point less than 110°C, preferably from 70°C to 110°C,

(b) polymerizing at least one second homogeneous ethylene/alpha-olefin interpolymer using a second constrained geometry catalyst having a second reactivity such that the second ethylene/alpha-olefin interpolymer has from 2 to 10 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point greater than 115°C, preferably from 115°C to 130°C, and

(c) combining from 50 to 95 weight percent of the first ethylene/alpha-olefin interpolymer with from 5 to 50 weight percent of the second ethylene/alpha-olefin interpolymer to form an ethylene/alpha-olefin interpolymer product.

When the interpolymers made in steps (a) and (b) are combined, an ethylene/alpha-olefin interpolymer product is formed having from 5 to 20 weight percent comonomer content, a melt index of from 0.5 to 50 grams/10 minutes, and an I_{10}/I_2 ratio of from 6 to 12 and, preferably, an M_w/M_n of from 2 to 6, and especially from 3 to 6. More preferably, the first homogeneous ethylene/alpha-olefin interpolymer made in step (a) has a narrow molecular weight distribution (NMWD) (i.e., $2 \leq M_w/M_n \leq 5$ with a very high comonomer content (i.e., $10 \leq \text{comonomer content} \leq 30$) and relatively high molecular weight (i.e., $0.05 \leq I_2 \leq 5$) and the second homogeneous ethylene/alpha-olefin interpolymer made in step (b) has a NMWD (i.e., $2 \leq M_w/M_n \leq 5$) with a low comonomer content (i.e., $2 \leq \text{comonomer content} \leq 6$) and a molecular weight lower than that of the first interpolymer.

The use of the dual reactivity constrained geometry catalysts can produce interpolymer products that satisfy a variety of requirements such as:

- (i) improved nucleation of polymers by adding a medium molecular weight, linear fraction, polyethylene;
- (ii) improved cling potential for stretch-cling polymers by producing an interpolymer fraction with a low molecular weight (MW) and high branch content;
- (iii) improved ultra low density polyethylene (ULDPE) by making a high MW fraction with a medium branch content which would improve film properties but not increase hexane extractables;
- (iv) improved optical properties (for example, clarity and haze), even for thermally formed articles made from the interpolymer products having higher densities; and
- (v) higher modulus of thermally formed articles made from the interpolymer product blends.

The interpolymer products made by polymerizing in two separate reactors and subsequently combining melt streams (parallel reactors) yields composite interpolymer product blends. At least one part of the composite interpolymer product blend, preferably from about 20-80 percent of the blend, has a melting point less than about 115°C, while at least another part of the blend has a melting point greater than about 120°C.

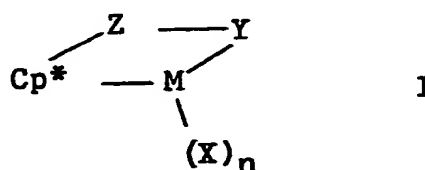
Constrained geometry catalyst preparation is described in detail in United States Application Serial Numbers 401,345 and 401,344, both filed August 31, 1989; SN 428,082, SN 428,283 and SN 428,276, all filed October 27, 1989; SN 436,524, filed November 14, 1989; SN 545,403, filed July 3, 1990; and SN 776,130, filed October 15, 1991. The disclosures of all of these U.S. Applications are incorporated herein by reference.

Suitable catalysts for use herein preferably include constrained geometry catalysts as disclosed in U.S. Application Serial Nos.: 545,403, filed July 3, 1990; 758,654, filed September 12, 1991; 758,660, filed September 12, 1991; and 720,041, filed June 24, 1991, the teachings of all of which are incorporated herein by reference. The monocyclopentadienyl transition metal

olefin polymerization catalysts taught in USP 5,026,798, the teachings of which are incorporated herein by reference, are also suitable for use in preparing the polymers of the present invention.

The foregoing catalysts may be generally further described as comprising a metal coordination complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements, preferably a metal of groups 3-6, and especially a metal of groups 4 and 5, and a delocalized π -bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted π -bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π -bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π -bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π -bonded moiety. The catalyst further comprises an activating cocatalyst.

Preferred catalyst complexes correspond to the formula:



wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

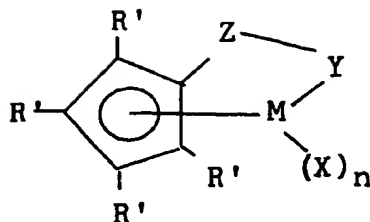
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

Y is an anionic or nonanionic ligand group bonded to Z and M comprising nitrogen, phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system.

M re preferably still, such complexes correspond to the formula:



wherein R' each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms;

X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, neutral Lewis base ligands and combinations thereof having up to 20 non-hydrogen atoms;

Y is -O-, -S-, -NR*, -PR*, or a neutral two electron donor ligand selected from the group consisting of OR*, SR*, NR*₂, or PR*₂;

M is a previously defined; and

Z is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR* = CR*, CR*₂SiR*₂, GeR*₂, BR*, BR*₂; wherein:

R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and

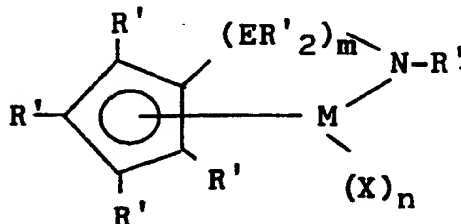
n is 1 or 2.

It should be noted that whereas formula I and the following formulas indicate a cyclic structure for the catalysts, when Y is a neutral two electron donor ligand, the bond between M and Y is more accurately referred to as a coordinate-covalent bond. Also, it should be noted that the complex may exist as a dimer or higher oligomer.

Further preferably, at least one of R', Z, or R* is an electron donating moiety.

Thus, highly preferably Y is a nitrogen or phosphorus containing group corresponding to the formula -N(R'')- or -P(R'')-, wherein R'' is C₁₋₁₀ alkyl or aryl, i.e., an amido or phosphido group.

Most highly preferred complex compounds are amidosilane- or amidoalkanedial- compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

5 E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, aryl, aryloxy or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2.

10 Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, 15 pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc. Specific compounds include: (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)methylene- 20 titanium dichloride, (tert-butylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dichloride, (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl, (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dimethyl, and the like. 25

The complexes may be prepared by contacting a derivative of a metal, M, and a group I metal derivative or Grignard derivative of the cyclopentadienyl compound in a solvent and separating the salt byproduct. Suitable solvents for use in preparing the metal complexes are aliphatic or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane, 30 heptane, tetrahydrofuran, diethyl ether, benzene, toluene, xylene, ethylbenzene, etc., or mixtures thereof.

In a preferred embodiment, the metal compound is MX_{n+1} , that is M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to 35 raise the oxidation state of the metal. The oxidation is accomplished merely by contacting the reactants utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "noninterfering oxidizing agent" is meant a compound having an oxidation potential sufficient to raise the metal oxidation state without interfering with the desired

complex formation or subsequent polymerization processes. A particularly suitable noninterfering oxidizing agent is AgCl or an organic halide such as methylene chloride. The foregoing techniques are disclosed in U.S. Ser. Nos.: 545,403, filed July 3, 1990 and 702,475, filed May 20, 1991, the teachings of both of which are incorporated herein by reference.

5 Additionally the complexes may be prepared according to the teachings of the copending application entitled: "Preparation of Metal Coordination Complex (I)", filed in the names of Peter Nickias and David Wilson, on October 15, 1991 and the copending application entitled: "Preparation of Metal Coordination Complex (II)", filed in the names of Peter Nickias and David Devore, on October 15, 1991, the teachings of which are incorporated herein by
10 reference thereto.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Preferred catalyst compositions are formed using cocatalysts which are inert, noncoordinating, boron compounds.

15 Ionic active catalyst species which can be used to polymerize the polymers described herein correspond to the formula:



wherein:

25 M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

30 Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

35 A⁻ is a noncoordinating, compatible anion.

One method of making the ionic catalyst species which can be utilized to make the polymers of the present invention involve combining:

a) at least one first component which is a mono(cyclopentadienyl) derivative of a metal of Group 3-10 or the Lanthanide Series of the Periodic Table of the Elements containing at least one substituent which will combine with the cation of a second component (described hereinafter) which first component is capable of forming a cation formally having a coordination number that is one less than its valence, and

b) at least one second component which is a salt of a Bronsted acid and a noncoordinating, compatible anion.

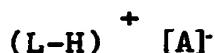
More particularly the noncoordinating, compatible anion of the Bronsted acid salt may comprise a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and non-nucleophilic. The recitation "metalloid", as used herein, includes non-metals such as boron and phosphorus which exhibit semi-metallic characteristics.

Illustrative, but not limiting examples of monocyclopentadienyl metal components (first components) which may be used in the preparation of cationic complexes are derivatives of titanium, zirconium, vanadium, hafnium, chromium, lanthanum, etc. Preferred components are titanium or zirconium compounds. Examples of suitable monocyclopentadienyl metal compounds are hydrocarbyl-substituted monocyclopentadienyl metal compounds such as (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyl-zirconium dimethyl, (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dibenzyl, (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)methylene-titanium dimethyl, (tert-butylamido)dibenzyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-titanium diphenyl, (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dibenzyl, and the like.

Such components are readily prepared by combining the corresponding metal chloride with a dilithium salt of the substituted cyclopentadienyl group such as a cyclopentadienyl-alkanediyl-amide, or cyclopentadienyl-silane amide compound. The reaction is conducted in an inert liquid such as tetrahydrofuran, C_{5-10} alkanes, toluene, etc. utilizing conventional synthetic procedures. Additionally, the first components may be prepared by reaction of a group II derivative of the cyclopentadienyl compound in a solvent and separating the salt by-product. Magnesium derivatives of the cyclopentadienyl compounds are preferred. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. The resulting metal cyclopentadienyl halide complexes may be alkylated using a variety of techniques. Generally, the metal cyclopentadienyl alkyl or aryl complexes may be prepared by alkylation of the metal cyclopentadienyl halide complexes with alkyl or aryl derivatives of group I or group II metals.

Preferred alkylating agents are alkyl lithium and Grignard derivatives using conventional synthetic techniques. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. A preferred solvent is a mixture of toluene and tetrahydrofuran.

- 5 Compounds useful as a second component in the preparation of the ionic catalysts useful in this invention will comprise a cation, which is a Bronsted acid capable of donating a proton, and a compatible noncoordinating anion. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the
- 10 Group 3-10 or Lanthanide Series cation) which is formed when the two components are combined and sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Suitable metals, then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like.
- 15 Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.
- 20 Highly preferably, the second component useful in the preparation of the catalysts of this invention may be represented by the following general formula:



25 wherein:

L is a neutral Lewis base;
 (L-H)⁺ is a Bronsted acid; and
 [A]⁻ is a compatible, noncoordinating anion.
 More preferably [A]⁻ corresponds to the formula:



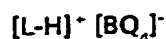
30 wherein:

M' is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements; and

Q independently each occurrence is selected from the Group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide and

q is one more than the valence of M'.

Second components comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



5 wherein:

L is a neutral Lewis base;

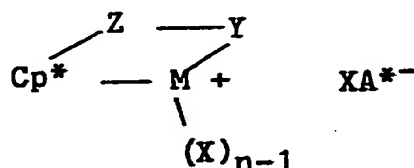
$[L-H]^+$ is a Bronsted acid;

B is boron in a valence state of 3; and

Q is as previously defined.

10 Illustrative, but not limiting, examples of boron compounds which may be used as a second component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetrphenylborate, tripropylammonium tetrphenylborate, tris(n-butyl)ammonium tetrphenylborate, trimethylammonium tetrakis(p-tolyl)borate, tributylammonium
15 tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(2,4-dimethylphenyl)borate, tributylammonium tetrakis(3,5-dimethylphenyl)borate, triethylammonium tetrakis(3,5-difluoromethylphenyl)borate and the like. Also suitable are N,N-dialkylanilinium salts such as N,N-dimethylanilinium tetrphenylborate, N,N-diethylanilinium tetrphenylborate, N,N-2,4,6-pentamethylanilinium tetrphenylborate and the like; dialkylammonium salts such as di-(i-
20 propyl)ammonium tetrakis(pentafluorophenyl)borate, dicyclohexylammonium tetrphenylborate and the like; and triaryl phosphonium salts such as triphenylphosphonium tetrphenylborate, tris(methylphenyl)phosphonium tetrakis(pentafluorophenyl)borate, tris(dimethylphenyl)phosphonium tetrphenylborate and the like.

Preferred ionic catalysts are those having a limiting charge separated structure
25 corresponding to the formula:



30

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wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

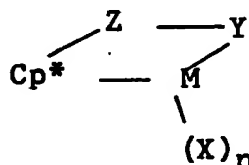
Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

XA* is $\text{XB}(\text{C}_6\text{F}_5)_3$.

This class of cationic complexes may be conveniently prepared by contacting a metal compound corresponding to the formula:



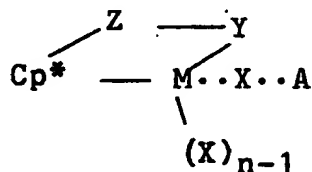
wherein:

Cp*, M, and n are as previously defined,

with tris(pentafluorophenyl)borane cocatalyst under conditions to cause abstraction of X and formation of the anion $\text{XB}(\text{C}_6\text{F}_5)_3$.

Preferably X in the foregoing ionic catalyst is C_1 - C_{10} hydrocarbyl, most preferably methyl.

The preceding formula is referred to as the limiting, charge separated structure. However, it is to be understood that, particularly in solid form, the catalyst may not be fully charge separated. That is, the X group may retain a partial covalent bond to the metal atom, M. Thus, the catalysts may be alternately depicted as possessing the formula:



The catalysts are preferably prepared by contacting the derivative of a Group 4 or Lanthanide metal with the tris(pentafluorophenyl)borane in an inert diluent such as an organic liquid. Tris(pentafluorophenyl)borane is a commonly available Lewis acid that may be readily prepared according to known techniques. The compound is disclosed in Marks, et al. J. Am. Chem. Soc. 1991, 113, 3623-3625 for use in alkyl abstraction of zirconocenes.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

It is believed that in the constrained geometry catalysts used herein the metal atom is forced to greater exposure of the active metal site because one or more substituents on the single cyclopentadienyl or substituted cyclopentadienyl group forms a portion of a ring structure including the metal atom, wherein the metal is both bonded to an adjacent covalent moiety and held in association with the cyclopentadienyl group through an η^5 or other π -bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is, the metal may be symmetrically or unsymmetrically π -bound to the cyclopentadienyl or substituted cyclopentadienyl group.

The geometry of the active metal site is further defined as follows. The centroid of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The angle, Θ , formed at the metal center between the centroid of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, Θ , is less than in a similar, comparative complex differing only in the fact that the constrain-inducing substituent is replaced by hydrogen have constrained geometry for purposes of the present invention. Preferably one or more of the above angles, Θ , decrease by at least 5 percent, more preferably 7.5 percent, compared to the comparative complex.

Preferably, monocyclopentadienyl metal coordination complexes of groups 3, 4, 5 or lanthanide metals according to the present invention have constrained geometry such that the angle, Θ , between the centroid of the Cp^* group and the Y substituent is less than 115° , more preferably less than 110° , most preferably less than 105° , and especially less than 100° .

Other compounds which are useful in the catalyst compositions of this invention, especially compounds containing other Group 4 or Lanthanide metals, will, of course, be apparent to those skilled in the art.

It is important that the specific constrained geometry catalysts chosen for polymerizing the ethylene polymers or ethylene/alpha-olefin interpolymers be of differing reactivities. The differing reactivities can be achieved by using the same constrained geometry catalyst composition, and polymerizing at different reactor temperatures, or, preferably, by using two distinctly different catalysts which have different reactivity. For example, when the active metal site is selected from the group consisting of Ti, V, Hf and Zr, the reactivity of the active metal site will be in that order: Ti is more reactive than V, which in turn is more reactive than Hf, which in turn is more reactive than Zr. Accordingly, the polymer density will also increase in that same order, with a polymer made using a constrained geometry catalyst containing Zr having a higher density than a polymer made using a constrained geometry catalyst containing Ti. Obviously, other combinations of metal atoms are possible, such as combining Ti with Hf, or combining V with Zr. The instant invention is not limited to any particular combination of constrained geometry catalysts, with the stipulation that the selected constrained geometry catalysts have differing reactivities.

In general, the polymerization according to the present invention may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired. A support may be employed but preferably the catalysts are used in a homogeneous manner. It will, of course, be appreciated that the active catalyst system, especially nonionic catalysts, form *in situ* if the catalyst and the cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

The polymerization conditions for manufacturing the polymers of the present invention are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Additives, such as anti-oxidants, slip agents, anti-block agents, pigments (for example, titanium dioxide), wetting agents (as disclosed, for example, in USP 4,578,414, and in USP 4,835,194, the disclosures of which are incorporated herein by reference) may be incorporated into the homogeneous polymers used to make the novel interpolymer products of the present invention to the extent that they do not interfere with the crystallization kinetic improvements demonstrated herein.

Fabricated (for example, thermally formed) articles can be advantageously made from these novel interpolymer products. These articles include films (for example, blown films,

cast films, or extrusion coated films), molded articles (for example, injection molded, blow molded, or rotomolded articles), and fibers (for example, melt blown, spunbond, or staple fibers and fabrics made from these fibers). Skilled artisans in the processability of conventional thermoplastics can readily form a variety of fabricated articles from these interpolymer products. In particular, the increased onset of crystallization temperature of these novel interpolymer products has utility in making fabricated articles which are rapidly cooled, for example, blown film (control of the freeze line) or melt spun fibers (where the high surface area of the fibers and the limited quench air capabilities are often in conflict).

The whole interpolymer product samples and the individual interpolymers samples are analyzed by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratories 10^3 , 10^4 , 10^5 , and 10^6), operating at a system temperature of 140°C . The solvent is 1,2,4-trichlorobenzene, from which 0.3% percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliter/minute and the injection size is 200 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Word in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968, incorporated herein by reference) to derive the equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , is calculated in the usual manner according to the formula:

$$M_w = \sum w_i * M_i$$

where w_i and M_i are the weight fraction and molecular weight respectively of the i th fraction eluting from the GPC column.

The crystallization onset temperatures of the blend components (i.e., the homogeneous polymers and interpolymers) and of the polymer and interpolymer products of the present invention are measured using differential scanning calorimetry (DSC). Each sample to be tested is made into a compression molded test plaque according to ASTM D 1928. The plaques are then microtomed at room temperature using a Reichert Microtome or razor blade to obtain samples having a thickness of about 15 microns. About 5 milligrams of each sample to be tested is placed in the DSC pan and heated to about 180°C , held at that temperature for 3 minutes to destroy prior heat history, cooled to -50°C at a rate of $10^\circ\text{C}/\text{minute}$ and held at that temperature for 2 minutes. The crystallization onset temperature and the peak temperature are recorded by the DSC as the temperature at which crystallization begins and the temperature at which the sample is as fully crystallized as possible, respectively, during the

cooling period from 180°C to -50°C. The sample is then heated again from -50°C to 140°C at a rate of 10°C/minute to record the heat of fusion and calculate total percent crystallinity. For polyethylene, the percentage crystallinity is obtained using the latent heat of fusion equal to 292 Joules/gram for 100 percent crystalline linear polyethylene.

5 Preparation of (t-Butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride

Step 1

(Chloro)(dimethyl)(tetramethylcyclopentadi-2,4-enyl)silane

To a solution of 21.5 g (167 mmol) dimethyldichlorosilane in 150 mL THF cooled to
10 -40°C was slowly added a solution of 8.00 g (55.6 mmol) sodium 1,2,3,4-tetramethylcyclopentadienide in 80 mL THF. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil.

15 Step 2

(t-Butylamino)(dimethyl)(tetramethylcyclopentadi-2,4-enyl)silane

A solution of 11.07 g (151 mmol) t-butyl amine in 20 mL THF was added during 5 minutes to a solution of 13.00 g (60.5 mmol) (chloro)(dimethyl)(tetramethylcyclopentadienyl)silane in 300 mL THF. A precipitate formed immediately. The slurry was stirred for
20 3 days, then the solvent was removed, the residue was extracted with pentane and filtered. The pentane was removed under reduced pressure to give the product as a light-yellow oil.

Step 3

Dilithium (tert-butylamido)(dimethyl)(tetramethylcyclopentadienyl)silane

To a solution of 3.000 g (11.98 mmol)
25 (t-Butylamino)(dimethyl)(tetramethylcyclopentadienyl)silane in 100 mL ether was slowly added 9.21 mL of 2.6 M (23.95 mmol) butyl lithium in mixed C₆ alkane solvent. A white precipitate formed and the reaction mixture was stirred overnight, then filtered. The solid was washed several times with ether then dried under reduced pressure to give the product as a white powder.

30 Step 4

(t-Butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride

0.721 g (3.80 mmol) Of TiCl₄ was added to 30 mL frozen (-196°C) THF. The mixture was allowed to warm to -78°C (dry ice bath). To the resulting yellow solution was slowly added
35 a solution of 1.000 g (3.80 mmol) dilithium (t-butylamido)(dimethyl)tetramethylcyclopentadienyl)silane in 30 mL THF. The solution was allowed to warm to room temperature while stirring overnight. The solvent was removed from the resulting very dark solution. The residue was extracted with pentane and filtered. Cooling in a freezer caused the

separation of a very soluble dark reddish-brown material from a light yellow-green crystalline solid. The solid was filtered out and recrystallized from pentane to give the olive-green catalyst complex product.

5 Methylaluminoxane (obtained commercially from Schering AG and designated herein as MAO) 10 percent by weight in toluene, is used in the examples described herein as a cocatalyst together with the catalyst complex to form the activated Ti stock solution catalyst mixture. (Other MAO preparations are disclosed, for example, in USP 5,041,583, USP 5,041,584 and USP 5,041,585, the disclosures of which are incorporated herein by reference.) The catalyst composition mixture is mixed for a few minutes and transferred by syringe to a catalyst
10 injection cylinder on the polymerization reactor.

 The compositions described in Table 2 are prepared with the same Ti stock solution and varying amounts of MAO solution and isoparaffinic solvent. Table 3 shows examples of a zirconium catalyst prepared in a similar manner from an equivalent complex ($[Zr] = 0.005 \text{ M}$) and the same MAO stock solution.

15 A stirred, one-gallon (3.79L) autoclave reactor is charged with two liters of an isoparaffinic hydrocarbon (Isopar™ E made by Exxon) and the alpha-olefin comonomer before heating to the temperature specified in Table 1. Hydrogen (10 mmol) is then added to the reactor, followed by ethylene sufficient to bring the total pressure to 450 pounds per square inch gauge (psig) (3204 kPa). An amount of the selected mixed constrained geometry activated
20 catalyst mixture, as described under the catalyst complex preparation section herein, is injected into the reactor. The reactor temperature and pressure are maintained constant at the desired final pressure and temperature by continually feeding ethylene during the polymerization run and cooling the reactor as necessary. After a 10 minute reaction time, the ethylene is shut off and the hot solution transferred into a nitrogen-purged resin kettle. After drying, the samples
25 are then weighed to determine catalyst efficiencies followed by melt index (ASTM D-1238, condition 190°C/2.16 kg) and density (ASTM D-792) measurements. The polymerization reaction conditions specified in Table 1 are used for both sets of homogeneous copolymers listed in Tables 2 and 3.

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Table 1
Polymerization conditions for single catalyst runs

Ex.	Reactor Temp. (°C)	Octene (moles)	Hydrogen (mmol)	Al:M* Ratio
1 & 1A	150	2.5	10	500
2 & 2A	150	2.5	10	500
3 & 3A	130	1	10	500
4 & 4A	130	1	10	250
5 & 5A	130	1	10	100

*M = selected metal atom (e.g., Ti or Zr)

Properties of some of the homogeneous copolymers made by using only a titanium based constrained geometry catalyst are listed in Table 2, while properties of the homogeneous copolymers made by using only a zirconium based constrained geometry catalyst are listed in Table 3. Even though the comonomer 1-octene is added to each separate reaction, very little of the 1-octene is incorporated into the copolymer when the catalyst is a zirconium catalyst (indicated by higher interpolymer density), due to the lower reactivity of the zirconium catalyst. The copolymers made using the titanium based constrained geometry catalyst have lower densities, indicating higher incorporation of 1-octene and higher reactivity of the titanium catalyst.

Table 2
Copolymer properties
using titanium constrained geometry catalyst

Ex.	Titanium (mmol)	Density (g/cm ³)	I ₂ (g/10 min)	Melt Point (°C)	M _w	M _n	M _w /M _n
1	0.02	0.9130	13.6	94.7	51000	14000	3.64
2	0.02	0.9121	10.1	95.9	53700	14700	3.65
3	0.02	0.9198	0.18	108.8	105000	23200	4.53
4	0.02	0.9197	0.15	109.8	136000	29400	4.63
5	0.02	0.9153	0.15	104.9	146000	26300	5.55

Table 3
Copolymer properties
using zirconium constrained geometry catalyst

Ex.	Zirconium (mmol)	Density (g/cm ³)	Melt Index (g/10 min)	Melt Point (°C)	M _w	M _n	M _w /M _n
1A	0.020	0.9468	98.9	123.9	39800	7470	5.33
2A	NM	NM	NM	NM	NM	NM	NM
3A	0.005	0.9556	20.6	128.7	62200	14000	4.44
4A	0.010	0.9533	12.2	128.4	60100	16800	3.58
5A	0.020	0.9519	11.5	128.6	56900	17100	3.33

NM = Not Measured

The constrained geometry catalysts can be used to polymerize the interpolymer products of the present invention in multiple reactor configurations as well. For example, one constrained geometry catalyst can be injected into one reactor and another constrained geometry catalyst having a different reactivity injected into another reactor. Or, the same constrained geometry catalyst can be injected into more than one reactor and the reactors operated at differing temperatures to effect differing catalyst reactivities.

Such multiple reactor schemes are well known to those skilled in the art of ethylene interpolymerization. For example, series and parallel dual reactor polymerizations are disclosed in USP 3,914,342, the disclosure of which is incorporated herein by reference.

A stirred, one-gallon (3.79L) autoclave reactor is charged with two liters of an isoparaffinic hydrocarbon (for example, Isopar[®] E made by Exxon) and the selected alpha-olefin comonomer before heating to the temperature specified in Table 4. Hydrogen (10 mmol) is then added to the reactor, followed by ethylene sufficient to bring the total pressure to 450 pounds per square inch gauge (psig) (3204 kPa). An amount of the mixed constrained geometry activated catalyst mixture (as described under catalyst activation) is injected into the reactor. The reactor temperature and pressure are maintained constant at the desired final pressure and temperature by continually feeding ethylene during the polymerization run and cooling the reactor as necessary. After a 10 minute reaction time, the ethylene is shut off and the hot solution transferred into a nitrogen-purged resin kettle. After drying, the samples are then weighed to determine catalyst efficiencies followed by melt index and density measurements.

Examples 6-12 are examples of ethylene/1-octene polymerizations performed in a single reactor, using a single injection of an activated mixture of constrained geometry catalysts (titanium and zirconium) at a methylaluminoxane (MAO):total catalyst metal ratio of

500:1 and are described in Table 4. Surprisingly, compression molded films made from the novel interpolymer product of Example 10 had a specular transmission (i.e., clarity) (ASTM D 1746) of about 4, while for compression molded films made from the novel interpolymer product of Examples 11 and 12, the specular transmission was less than about 1. The higher reactor polymerization temperature used to make the interpolymer product of Example 10 (160°C) therefore improves the specular transmission of film made therefrom, especially when compared with the film made from interpolymer products polymerized at temperatures lower than about 160°C.

Example 13 is a comparative example using only a single constrained geometry catalyst (MAO:Ti ratio of 500:1) at a single reaction temperature (110°C).

Example 14 illustrates the use of a single activated constrained geometry (Titanium at MAO:Ti ratio of 500:1) catalyst at two different reactor temperatures (110°C and 150°C).

Examples 15-19 show ethylene/1-octene interpolymerizations using mixed constrained geometry catalysts (Ti and Zr) at MAO:total metal concentrations of 350:1.

Examples 20-22 show data relating to interpolymerizations of ethylene with tetradecene, octadecene and cyclooctene, respectively. For Examples 20 and 21, the MAO:total metal concentration is 500:1 while for Example 22 the MAO: total metal concentration is 750:1.

Examples 23-25 describe ethylene/1-propene/1-octene terpolymer interpolymerizations, each using a single injection of a mixture of two constrained geometry catalysts (titanium and zirconium), each using methylaluminoxane as a cocatalyst to form the activated catalyst mixture.

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Table 4
Polymerizations using 2 constrained geometry catalysts having differing reactivities

Ex.	1-octene (ml)	H ₂ (mmol)	mmole Ti	mmole Zr	Ti:Zr ratio	Reactor Temp. (°C)	Sample Weight (grams)	Gradient Density (g/cm ³)	I ₂ (g/10 min)	I ₁₀ /I ₂	Cryst. Onset (°C)	$\frac{M_w}{M_n}$
6	150	10	.016	.004	4:1	130	180	.9280	.7	13.4	112.8	4.81
7	150	10	.0121	.008	3:2	130	180	.9392	1.5	12.3	114.8	4.57
8	300	10	.0046	.016	3.5:1	130	190	.9434	13.2	7.5	114.8	3.22
9	300	10	.008	.002	4:1	130	172	.9261	2.5	10.3	113.5	4.13
10	150	10	.0093	.00125	8:1	160	40	.9367	NM*	NM*	113.3	3.64
11	150	20	.0093	.00125	8:1	130	128	.9260	3.8	9.7	112.7	3.64
12	150	30	.0093	.00125	8:1	100	218	.9250	10.3	7.2	114.5	2.66
13 ^c	150	20	.02	0	0	110	209	.9136	.2	15.6	96.3	3.89
14***	150	40	.012	0	0	110/150	172	.9236	13.1	7.2	108.1	2.43
15**	150	30	.019	.001	20:1	130	188	.9195	NM	NM	99.8	NM
16**	150	30	.019	.001	20:1	162	82	NM	NM	NM	104.1	NM
17**	150	10	.019	.001	20:1	160	70	.9290	NM	NM	105.2	NM
18**	150	30	.0095	.0005	20:1	100	105	NM	NM	NM	95.9	NM
19**	150	20	.019	.001	20:1	100	225	.9120	NM	NM	94	NM

MAO: total metal ratio for Examples 6-14 = 500:1

*NM = Not Measured

**MAO:total metal ratio for Examples 15-19 = 350:1

***Half of the catalyst is injected at reactor temp. of 110°C,

then the reactor temp was increased to 150°C and the other half of the catalyst injected

^c = Comparative Example only

Table 5
Polymerizations using comonomers other than 1-octene
using 2 constrained geometry catalysts having differing reactivities

Ex.	Comonomer (ml added)	mmole Ti	mmole Zr	Ti:Zr ratio	Reactor Temp. (°C)	Sample Weight (grams)	Gradient Density (g/cm ³)	I ₂ (g/10 min)	MAO: soluble Ti	Cryst. Onset (°C)	M _w /M _n
20	tetradecene (300)	.019	.001	19:1	130	275	.9245	96.8	500:1	96.8	2.86
21	octadecene (300)	.019	.001	19:1	130	250	.9166	45.1	500:1	104.9	3.91
22	cyclooctene (350)	.019	.001	19:1	130	150	.9265	32.3	750:1	121.3	3.65

Table 6
 Polymerizations of ethylene/1-propene/1-octene terpolymers
 using 2 constrained geometry catalysts having differing reactivities

Ex.	1-octene (ml)	1-propene (gm)	mmole Ti	mmole Zr	Ti:Zr ratio	Reactor Temp. (°C)	Sample Weight (grams)	Gradient Density (g/cm ³)	I ₂ (g/10 min)	Cryst. Onset (°C)	M _w /M _n
23	150	40	.019	.001	19:1	130	75	.9051	NF*	103.7	4.62
24	150	20	.019	.001	19:1	140	75	.9158	7	109.2	4.52
25	150	10	.019	.001	19:1	150	75	.9273	21.8	108	4.05

*NF = No Flow (i.e., the molecular weight is very high)
 MAO : total metal = 500:1 for Ex. 23-25

CLAIMS

1. A process for preparing an ethylene polymer product, comprising the steps of:

(a) polymerizing a first homogeneous ethylene polymer using a first activated constrained geometry catalyst composition having a first reactivity such that the first polymer
5 has a melt index of from 0.05 to 50 grams/10 minutes,

(b) polymerizing at least one second homogeneous ethylene polymer using a second activated constrained geometry catalyst composition having a second reactivity such that the second ethylene polymer has a melt index of from 0.05 to 50 grams/10 minutes, and

(c) combining from 50 to 95 weight percent of the first ethylene polymer with
10 from 5 to 50 weight percent of the second ethylene polymer to form an ethylene polymer product.

2. A process for preparing an ethylene/alpha-olefin interpolymer product, comprising the steps of:

(a) polymerizing a first homogeneous ethylene/alpha-olefin interpolymer using a
15 first activated constrained geometry catalyst composition having a first reactivity such that the first interpolymer has from 5 to 30 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point less than about 110°C,

(b) polymerizing at least one second homogeneous ethylene/alpha-olefin interpolymer using a second activated constrained geometry catalyst composition having a
20 second reactivity such that the second ethylene/alpha-olefin interpolymer has from 2 to 10 weight percent comonomer content, a melt index of from 0.05 to 50 grams/10 minutes, a melting point greater than about 115°C, and

(c) combining from 50 to 95 weight percent of the first homogeneous ethylene/alpha-olefin interpolymer with from 5 to 50 weight percent of the second
25 homogeneous ethylene/alpha-olefin interpolymer to form an ethylene/alpha-olefin interpolymer product.

3. The process of Claims 1 or 2 wherein the first activated constrained geometry catalyst composition comprises a titanium constrained geometry complex and an aluminoxane cocatalyst.

4. The process of Claims 1 or 2 wherein the second activated constrained geometry catalyst composition comprises a zirconium constrained geometry complex and an aluminoxane cocatalyst.
5. The process of Claims 1 or 2 wherein the second activated constrained geometry catalyst composition comprises a zirconocene constrained geometry complex and an aluminoxane cocatalyst.
6. The process of Claim 2 wherein (a) and (b) are performed substantially simultaneously in a common reactor.
7. The process of Claim 6 further comprising the steps of:
 - (d) mixing the first and second catalyst compositions together to form a catalyst mixture, and
 - (e) injecting the catalyst mixture into the common reactor.
8. The process of Claim 2 wherein (a) and (b) are performed separately in at least two reactors.
9. The process of Claim 8 wherein the two reactors comprise at least a first reactor and a second reactor and wherein the two reactors are operated in series.
10. The process of Claim 8 wherein the two reactors are operated in parallel.
11. The process of Claim 2 wherein the homogeneous ethylene/alpha-olefin interpolpolymer produced in step (a) has a melting point from 70°C to 110°C and wherein the homogeneous ethylene/alpha-olefin interpolpolymer produced in step (b) has a melting point from 115°C to 130°C.
12. The process of Claim 2 wherein at least one of the alpha-olefins is a C₂-C₁₈ alpha-olefin.
13. The process of Claim 12 wherein at least one of the alpha-olefins is selected from the group consisting of ethylene, 1-propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene.
14. The process of Claim 13 wherein the first and the second ethylene/alpha-olefin interpolpolymer each comprises a copolymer of ethylene and 1-octene.
15. The process of Claim 2 wherein either the first or the second activated constrained geometry catalyst compositions, or both, are chosen from constrained geometry catalyst components selected from the group consisting of titanium, vanadium, hafnium and zirconium.
16. The interpolpolymer product of Claim 2 wherein the first homogeneous ethylene/alpha-olefin interpolpolymer and the second homogeneous ethylene/alpha-olefin interpolpolymer are combined in amounts effective to yield an interpolpolymer product having a crystallization onset temperature at least about 5°C higher than the crystallization onset temperature of the interpolpolymer produced by the activated constrained geometry catalyst composition having the higher reactivity.

17. The interpolymer product of Claim 2 wherein the first homogeneous ethylene/alpha-olefin interpolymer and the second homogeneous ethylene/alpha-olefin interpolymer are combined in amounts effective to yield a crystallization onset temperature of at least about 110°C.

5 18. The interpolymer product of Claim 2 wherein the first and the second ethylene/alpha-olefin interpolymer each comprises a copolymer of ethylene and 1-octene.

19. A fabricated article made from the interpolymer product of Claim 16.

20. The fabricated article of Claim 19 selected from the group consisting of films, molded articles, and fibers.

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FIG. 1

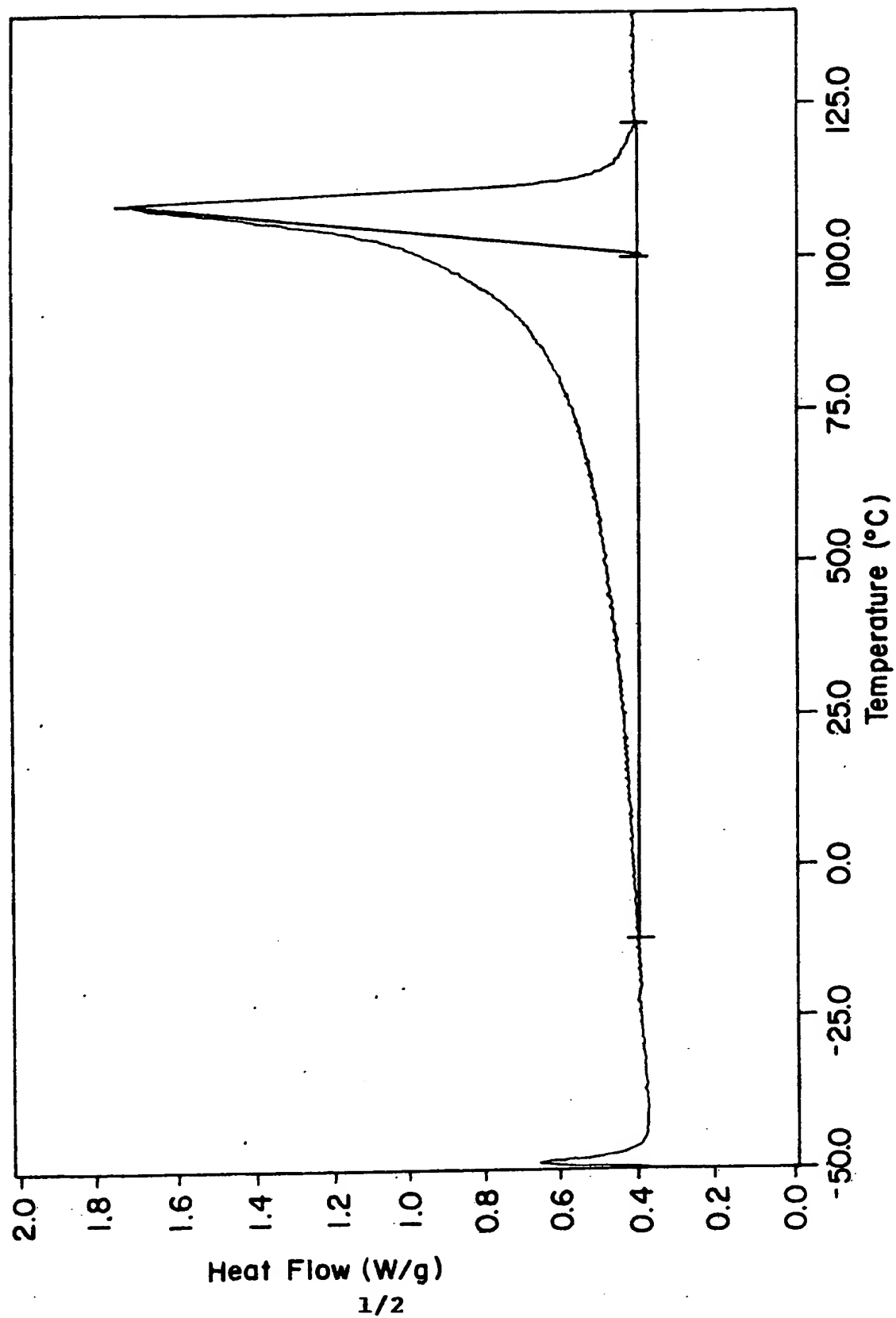
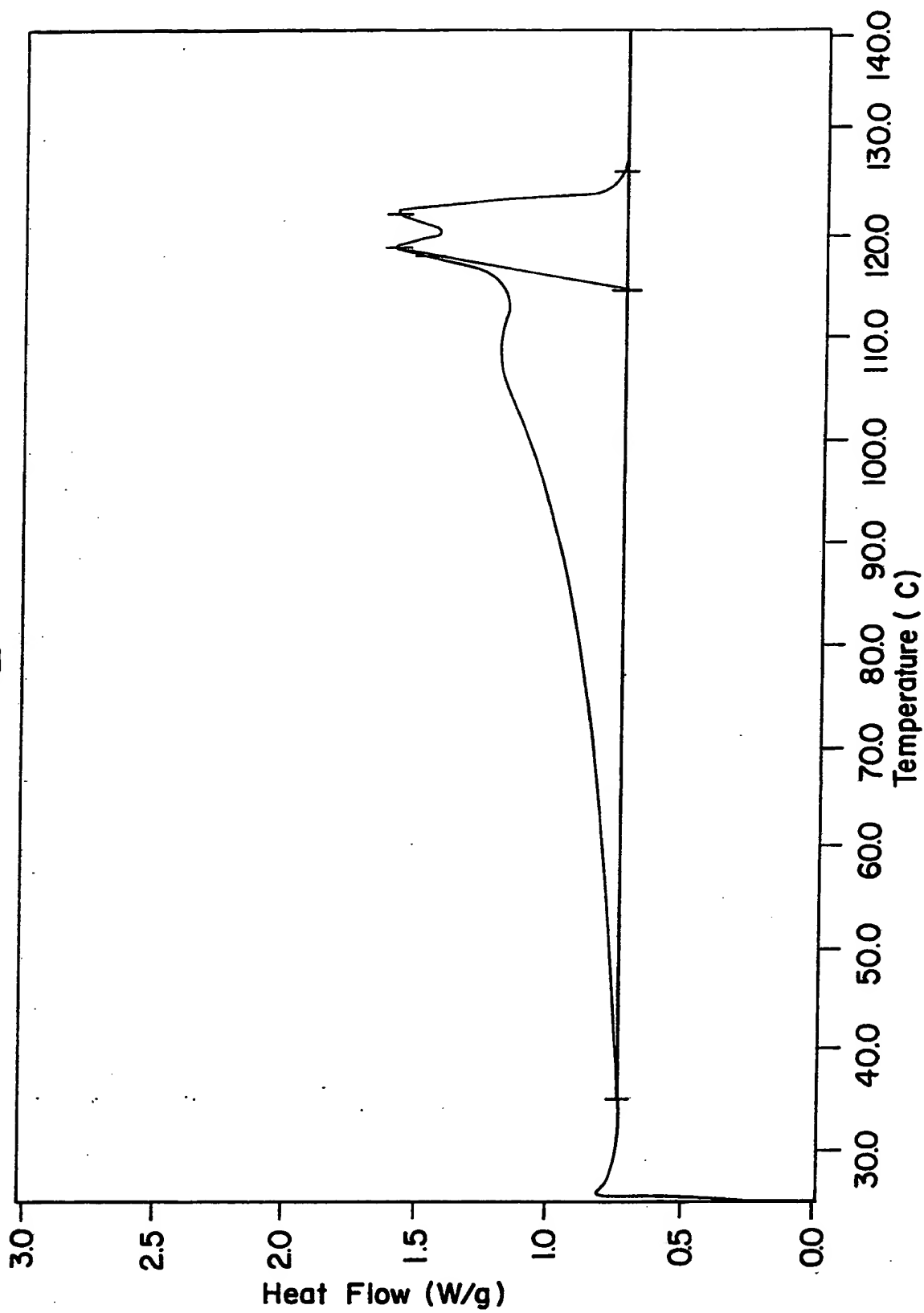


FIG.2



I. CLASSIFICATION F SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08F10/02; C08F297/08											
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">Int.Cl. 5</td> <td style="padding: 5px;">C08F</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched⁸</div>			Classification System	Classification Symbols	Int.Cl. 5	C08F					
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Int.Cl. 5	C08F										
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category⁹</th> <th style="border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 10%; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> EP,A,0 128 046 (EXXON RESEARCH AND ENGINEERING COMPANY) 12 December 1984 see the whole document & US,A,4 937 299 (cited in the application) <div style="text-align: center;">---</div> </td> <td></td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> EP,A,0 416 815 (THE DOW CHEMICAL COMPANY) 13 March 1991 see claims 1-25 & US,P,401 345 (cited in the application) <div style="text-align: center;">-----</div> </td> <td></td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	EP,A,0 128 046 (EXXON RESEARCH AND ENGINEERING COMPANY) 12 December 1984 see the whole document & US,A,4 937 299 (cited in the application) <div style="text-align: center;">---</div>		A	EP,A,0 416 815 (THE DOW CHEMICAL COMPANY) 13 March 1991 see claims 1-25 & US,P,401 345 (cited in the application) <div style="text-align: center;">-----</div>	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>⁹ Special categories of cited documents :¹⁰</p> <p>^{"A"} document defining the general state of the art which is not considered to be of particular relevance</p> <p>^{"E"} earlier document but published on or after the international filing date</p> <p>^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>^{"O"} document referring to an oral disclosure, use, exhibition or other means</p> <p>^{"P"} document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>^{"A"} document member of the same patent family</p> </div> </div>											
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">13 APRIL 1993</div> </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">17. Oct. 93</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center;">EUR PEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;">FISCHER B.R.</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">13 APRIL 1993</div>	Date of Mailing of this International Search Report <div style="text-align: center;">17. Oct. 93</div>	International Searching Authority <div style="text-align: center;">EUR PEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">FISCHER B.R.</div>					
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9211269
SA 68680

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU-A- 2910784	13-12-84
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